

3.3 Strategies to Prevent Autocatalytic Reactions

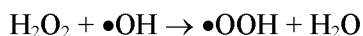
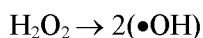
Autocatalytic reactions are possible when using Fenton's reagent due to the induction period necessary to build up sufficient hydroxide radicals to initiate reaction. During the course of preliminary beaker testing, any tendency for autocatalytic reaction was evident from the results of the experiments. These observations of autocatalytic reactions provided qualitative data to support TO 8—To propose and provide data to support a detailed strategy to prevent autocatalytic reactions for Fenton's reagent during active remediation.

The Fenton's reagent reactions are:



from which the hydroxide and peroxide radicals react further to oxidize organic compounds to various extents.

The decomposition of hydrogen peroxide occurs through the reactions:



The decomposition reactions are autocatalytic because the products of the reactions participate in the reaction, and the rate accelerates as the concentration of the products increases.

When iron is present in solution with peroxide, at higher pH, Fe(OH)_3 will precipitate and catalyze the decomposition reaction, as described in:

(<http://www.h2o2.com/applications/industrialwastewater/fentonsreagent.html>).

When properly stored, hydrogen peroxide is stable. Primary factors that can cause an uncontrolled decomposition of hydrogen peroxide are temperature, pH, and contamination. Excessive contamination of hydrogen peroxide during storage, shipment, and handling can cause autocatalytic decomposition. Handling and storage recommendations are given below:

- Store in the original shipping container or properly designed containers.
- Do not return hydrogen peroxide to the container from which it was removed.
- Store away from heat sources.
- Properly vent storage containers and reaction vessels.
- Adequate ventilation and water supply should be available for spills (Ref. 12).

During the preliminary beaker tests performed in April 2003, there was one instance of reaction excursion. A summary of the beaker test is given below:

Feed:

Hydraulic oil:	1.503 g
Cutting oil:	1.507 g
DI water:	96.014 g
FeSO ₄ • 7H ₂ O:	2.002 g

Caustic used for pH control was in the range of 3 to 4.

Purpose:	To inject peroxide at a high rate (100 mL in 10 min) with additional iron in solution in an attempt to determine whether the solution would reach approximately 90°C, and remain in a band near there during the course of the run while injecting additional peroxide. After the initial large injection of peroxide, a maintenance dose of peroxide was to be injected at 2 mL/min. in an attempt to maintain temperature. The maintenance dose was to inject up to 200 mL additional peroxide.
Narrative:	<p>Injection was started at 10 mL/min. Almost immediately, vigorous foaming began. Two minutes into the run, the temperature rose from 40 to 57°C. At 3 min, the injection was halted due to overflow of the reaction beaker into the secondary containment beaker.</p> <p>The pH of the solution dropped significantly. In an attempt to control the pH decline, it may have been overdosed with caustic. The solution pH approached 7 after foaming quit. Both low pH and high pH will cause peroxide to effervesce oxygen, effectively killing the reaction.</p>

During the beaker test described above, more iron than the usual 1 g FeSO₄•7H₂O per 100 g of surrogate was added; however, the excursion was probably due to increasing pH from an excessive addition of caustic.

Another excursion was noted following the second shakedown run in the 1,000 mL stirred reaction beaker, test F2A (40°C, 400 mL, 8 hr). Prior to this excursion, it was assumed that the reaction products could be stabilized by using caustic to adjust the pH to around 7. When caustic was added to 300 mL of the product, the slurry began foaming vigorously, generated heat, and overflowed into a 2-L secondary containment beaker (MSE logbook 2, page 6).

The products from all of the 40°C runs have behaved similarly, and have been very difficult to prepare for SVOC analyses. The 40°C products all had residual peroxide in excess of 35% and reaction continued to occur at 4°C storage temperature within the sample bottles for many days after capping. Samples from F-6 (40°C, 500 mL, 8 hr) were received at the BWXT with substantially less volume than was prepared for shipment, indicating that concentration of the samples en route to the laboratory was reduced due to peroxide reacting to O₂.

During preliminary testing and SVOC sample preparations, excursions (it is unclear if the observations were actually autocatalytic) were noted when certain conditions were present, indicating the potential for autocatalytic reactions. The following recommendations are made to prevent autocatalytic reactions in the final process:

- Near neutral pH should be avoided when residual peroxide is present. When preparing samples from 40°C runs, the residual peroxide analysis indicated that a large amount of peroxide (>35% in most cases) was present after test completion. When samples for SVOC analysis with residual peroxide were neutralized to pH 6, excursions were encountered. The samples foamed and streamed out of the sample vials from the liberation of oxygen. In the final process, adjustment of the pH downward to 3–3.5 should be accomplished prior to addition of peroxide to the reaction vessel.
- Redundant block valves for caustic pH adjustment should be designed to prevent inadvertent addition of caustic to the system when peroxide is being fed, or when residual peroxide is present in the reaction vessel.
- Running at 80°C does not allow peroxide to accumulate to levels that would generate an autocatalytic reaction. Residual peroxide was much lower (<2%) after the 80°C test runs regardless of the amount of peroxide addition. A likely process step in the full-scale system will include running at a higher temperature to ensure that residual peroxide is not present prior to neutralization of the reaction products.

At test conditions explored to date, excursions have not been noted in the 1,000-mL flask and associated glassware being used to perform the experiments. This absence of excursions is probably due to cooling provided by the reaction vessel jacket/circulating fluid and the reflux condenser, as well as maintaining the pH at ~3.5. The laboratory apparatus and procedures, as designed for these test conditions, were successful in preventing autocatalytic behavior and excursions during test conduct.

3.4 Real-Time Methods to Identify Chemical Reaction Completion

The final test objective, TO 10, was “to determine completion of destruction of the RCRA hazardous organics and total organics. To identify real-time methods for determining completion points.” To support the second part of T10—to identify real-time methods for determining these completion points—data were collected as the experiments were ongoing. These parameters were compared with contaminant DRE results to determine whether real-time methods could indicate reaction completion.

Prior to testing, the following real-time measurements were targeted to support TO10:

- Chloride ion concentration in reactor contents
- E_H of reactor contents, the electrochemical potential of the solution, measured in volts
- Characterization of off-gas.

Monitoring of chloride ion concentration and E_H in real-time was not possible due to deterioration of probes used to perform the measurements and interfering species present in the surrogate. The only information left to support TO10 was off-gas characterization data. These data are only semi-real-time using the current experimental apparatus. During follow-on tests in FY-04, every effort will be made to collect real-time data for off-gas characterization. For the final test [F-22 (80°C, 600 mL H₂O₂, 12 hr)] an on-line oxygen/carbon dioxide meter was procured and provided the best real-time data for determining

oxidized. The best parameter to monitor to determine the progression of the chemical oxidation reaction is CO_2 in the off-gas.

3.4.1 Carbon Dioxide Off-Gas Analyses

Gas samples were collected using syringes at the outlet of the Dewar condenser and analyzed by GC/MS for carbon dioxide, TCA, TCE, and PCE. The water vapor content of these gas samples was assumed to be at saturation at the temperature read at the outlet of the reflux condenser. Oxygen content was calculated by difference. Carbon dioxide, carbon monoxide, and oxygen concentrations were also periodically monitored using industrial safety monitors and Draeger tubes for selected tests. The final test (F-22 [80°C, 600 mL H_2O_2 , 12 hr]) had a dedicated O_2/CO_2 analyzer for more frequent reading of O_2/CO_2 concentrations in the off-gas. This instrument analyzed for O_2 and CO_2 separately. Figure 3-4 shows the CO_2 generation versus time for selected tests, including F-22.

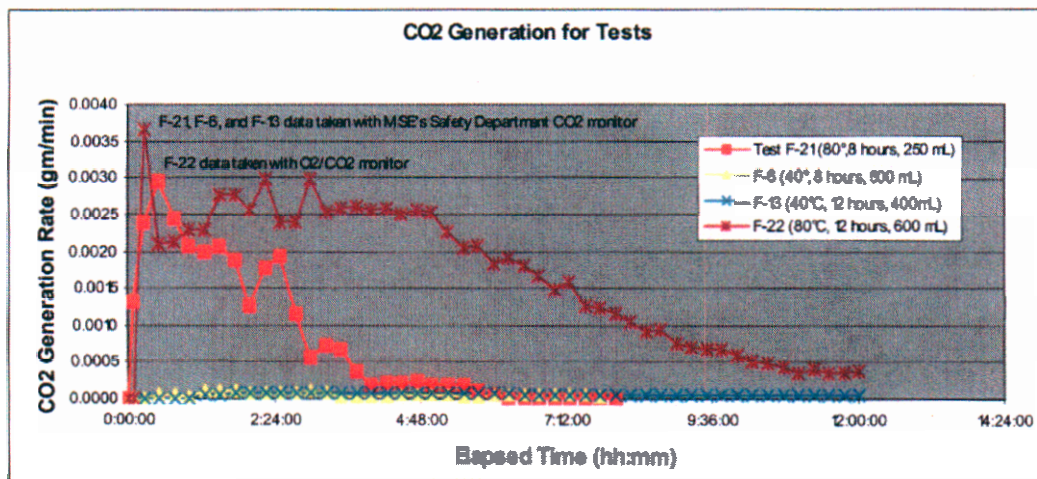


Figure 3-4. CO_2 generation profiles for selected tests.

It is clear from Figure 3-4 that the CO_2 generation for the 40°C tests was much lower than that for 80°C tests, for data collected using the safety CO_2 meter. Also, the O_2/CO_2 meter used for F-22 (80°C, 600 mL H_2O_2 , 12 hr) gave higher results when compared to the safety meter. The 40°C tests were not run when the O_2/CO_2 meter was available. Data from the O_2/CO_2 meter was assumed by MSE Technology to give the most reliable results; however, these results may also be biased low because the O_2/CO_2 meter is attempting to quantitate CO_2 concentrations at the low end of the meter's range. In any case, the downward trend of CO_2 after the addition of peroxide ceases for the 80°C runs indicates that monitoring CO_2 levels in the off-gas could provide a real-time means for monitoring the progression/completion of the reaction.

After the areas under the curves in Figure 3-4 are determined, the total amount of CO_2 generated for a particular test can be calculated. These results are summarized in Table 3-9.

Theoretically, about 14 g of CO_2 would be expected for complete mineralization of the organic components in the surrogate. The incomplete recovery of CO_2 can be explained by the residual oil observed in the reaction products after the test; by the incomplete destruction of the organic components and the likely formation of intermediates that remain in the reacted slurry. However, oil and grease and DRE measurements may indicate that most of the carbon has been removed from the product slurry, indicating uncertainty in the CO_2 analysis of the product gas.

Table 3-9. CO₂ generation summary for test with valid gas data.

Test Identifier	Conditions	CO ₂ generated (g)
F-6	40°C, 8 hr, 500 mL	0.026
F-13	40°C, 8 hr, 400 mL	0.061
F-21	80°C, 8 hr, 250 mL	0.54
F-22	80°C, 12 hr, 600 mL	1.7

Note: Test F-22 (80°C, 600 mL H₂O₂, 12 hr) data was collected using a dedicated CO₂/O₂ monitor. F-6 (40°C, 500 mL H₂O₂), F-13 (40°C, 400 mL H₂O₂, 12 hr), and F-21 (80°, 250 mL H₂O₂, 8 hr) data were collected using periodic measurements with a safety CO₂ monitor.

Process parameters that may also prove to be useful in determining how the reaction is proceeding include the following:

- Reactor temperature
- Bulk gas generation rate.

Because the results of the 80°C tests were much more promising, the analyses of data presented in the next two sections focus mainly on the 80°C test results.

3.4.2 Reactor Temperature

Reactor temperature was brought to the test temperature (80°C) prior to initiating the flow of peroxide. Reactor temperature was recorded every 15 minutes throughout each test. During the tests, temperatures in the reactor increased as the reaction proceeded. When a lower amount of peroxide was charged to the reactor, the temperature declined earlier in the test. The temperature of reactor contents could be used as an indicator that the peroxide present has been utilized or depleted, and that active treatment has ceased. Figure 3-5 summarizes the temperature profiles for the 80°C tests.

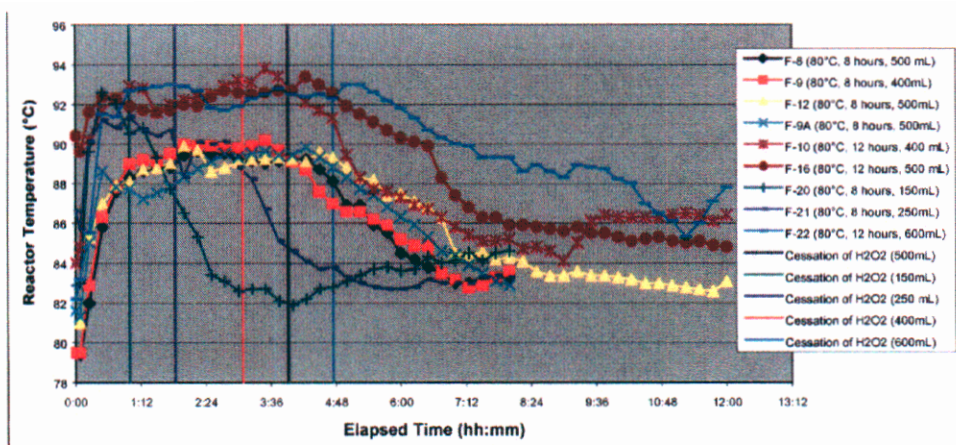


Figure 3-5. Temperature versus time for 80°C tests.

The temperature never returned to the initial temperature throughout the formal test durations; for some experiments, a temperature increase was noted at the end of the test (i.e., Tests F-10 [80°C, 400 mL H₂O₂, 12 hr], F-20 [80°C, 150 mL H₂O₂, 8 hr], and F-22 [80°C, 600 mL H₂O₂, 12 hr]). It is unclear if this increase was due to ambient temperature increase over the course of the day, or the result of continued

reaction. The temperature profiles for the 80°C tests also mirror the bulk gas generation rates for the 80°C tests, as described below.

3.4.3 Bulk Gas Generation Rate

The gas generation rate was measured using a bubble meter every 15 min during each test. Gas generation was higher during the periods when peroxide was being added to the reactor for 80°C tests. After peroxide addition ceased, the amount of gas generation slowly decreased until near the end of the 8-hr tests. For the final hour of the 12-hr tests, the gas generation was virtually zero, with the exception of test F-22 (80°C, 600 mL H₂O₂, 12 hr). As more peroxide was added for each test condition at 80°C, gas generation continued for a longer period, as predicted. This is illustrated in Figure 3-6. When gas generation reaches zero, it may indicate that active treatment has ceased. Because samples of the treated slurry were not collected after gas generation ceased, but rather up to 12 hr later, it is unclear whether treatment took place during periods with little or no gas generation. There was a general decay in the generation of gas. The run plan called for tests of this duration, and the plan was followed. The reaction may proceed beyond visible gas generation, and there was no reason to terminate the test prematurely.

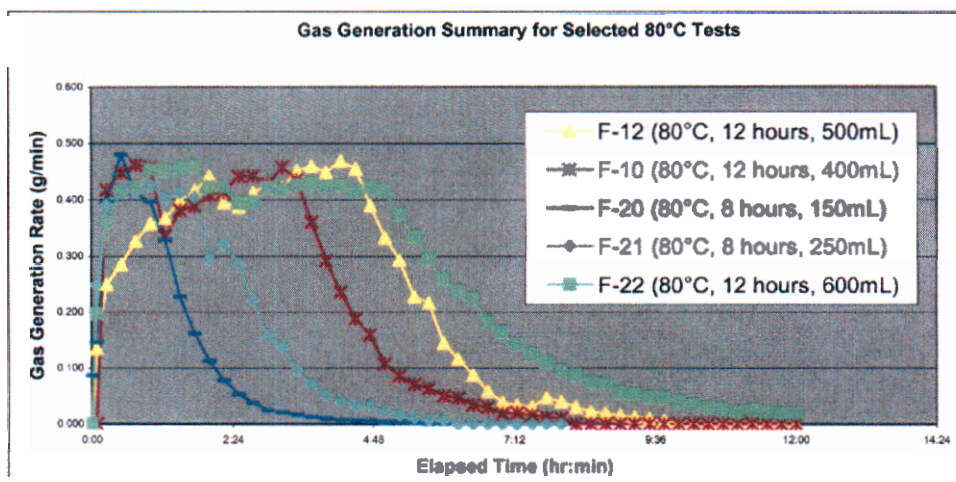


Figure 3-6. Bulk gas generation rate versus time for selected 80°C tests.

Test F-22 (80°C, 600 mL H₂O₂, 12 hr) was still producing gas when the test ceased. An increase in reactor temperature was also noted at the end of this test. By the following morning, gas generation had ceased. Continued gas generation at these test conditions may indicate that the reaction/active treatment was still ongoing; however, significantly higher DREs were not noted.

3.5 Stabilization of V-Tank Surrogate Waste

MSE Technology continued to evaluate the ability of the "B" and "E" grout formulations to meet RCRA UTS for mercury and total chromium in postoxidized V-tank waste surrogate. The TCLP levels indicating compliance with the UTS are 0.025 mg/L and 0.60 mg/L, respectively (Ref. 3). The reassessment of treatment effectiveness is necessitated by changes in both surrogate composition (e.g., phosphate addition) and oxidant (i.e., use of Fenton's reagent versus persulfate ion).

Given the results of previous treatability investigations by Richardson (Ref. 6) and MSE Technology (Ref. 13), use of the two most promising grout formulations was revisited. The composition of these mixtures is shown in Table 3-10.

Table 3-10. Grout formulations evaluated in this study.^a

“B” Mix		“E” Mix	
Component	Weight (g)	Component	Weight (g)
Portland Cement Type (PCT)-V/II	9.60	PCT-III	60.00
Fly ash	55.20	Silica fume	18.00
Slag	55.20	Slag	42.00
Total	120.00		120.00

Note: The PCT-V/II and PCT-III plus powdered furnace slag were provided by Lafarge North America; Class F fly ash from the Jim Bridger power plant was provided by ISG Resources; and Rheomac SF100 silica fume was provided by Master Builders, Inc.

The sources of cements, slag, and fly ash were the same as used previously; the silica fume was obtained directly from the same source as used previously by Lafarge North America. The ratio of 1.5 g grout mix to 1 mL surrogate slurry is the same as used previously; this translates to 80.0 mL of slurry being stirred into 120 g of solid.

Given the volume of liquid required for the grouting study and potential variability in slurry composition after Fenton’s treatment, MSE Technology also prepared a posttreatment surrogate slurry. Its composition represents a twofold dilution of the pretreatment surrogate due to water addition from decomposed hydrogen peroxide (H_2O_2). It also assumes complete conversion (oxidation) of elemental mercury and chromium oxide to soluble mercuric ion and chromate ion (including charged, neutral complexes), respectively.

Equal weights of cutting and hydraulic oils were reacted with 50% by weight H_2O_2 in quantities representing ca. 90:1 and 900:1 molar ratios of peroxide to oil. These ratios are taken to represent high residual oil and low residual oil, respectively, in treated tank waste. Aliquots of these reaction products were then added to the posttreatment surrogates; the compositions are tabulated in Table 3-11.

Table 3-11. High and low oil variants of the posttreatment surrogate slurry.

Component	Slurry Composition (g)	
	High Oil (90:1 moles H_2O_2 :Oil)	Low Oil (900:1 moles H_2O_2 :Oil)
DI water	335.586	368.155
Residual oil/ H_2O_2	103.488	70.923
$AlCl_3 \bullet 6HOH$	0.403	0.403
$CaCl_2 \bullet 2HOH$	0.803	0.802
$Cr(VI)O_3$	0.548	0.549
$FeCl_3 \bullet 6HOH$	2.323	2.323
$FeSO_4 \bullet 7HOH$	2.500	2.500
MgO	1.302	1.303
MnO	0.762	0.762
SiO_2	15.027	15.028

Table 3-11. (continued).

Component	Slurry Composition (g)	
	High Oil (90:1 moles H ₂ O ₂ :Oil)	Low Oil (900:1 moles H ₂ O ₂ :Oil)
Na ₃ PO ₄	21.955	21.955
KOH	0.577	0.570
Hg(II)Cl ₂	0.126	0.125
H ₂ SO ₄ (Concentrated) ^a	14.600	14.602
Total	500.000	500.000

a. To adjust pH ≤ 4.0.

3.5.1 Methods

Four separate aliquots of each grout formulation were prepared on June 30, 2003; the composition of each mixture is shown in Table 3-12.

The aliquots were stored in labeled, 230-mL capacity plastic (low-density polyethylene) cups with caps at room temperature until use.

Table 3-12. Compositions of the grout mixtures prepared in June 2003.

Part A. "B" Mixtures (g)				
Component	B1	B2	B3	B4
PCT-V/II	9.60	9.60	9.60	9.60
Fly ash	55.20	55.21	55.20	55.21
Slag	55.21	55.21	55.20	55.21
Total	120.01	120.02	120.00	120.02

Part B. "E" Mixtures (g)				
Component	E1	E2	E3	E4
PCT-III	60.01	60.00	60.07	60.01
Silica fume	18.03	18.00	18.07	18.02
Slag	42.04	42.03	42.10	42.07
Total	120.08	120.03	120.24	120.10

The first slurry/grout mixtures were prepared on the afternoon of June 30, 2003, via stirring approximately 80 mL of a particular slurry (e.g., low oil) into a particular grout cup (e.g., B2). Each mixture was stirred by hand, using a stainless steel spatula, until uniform in appearance. The mixtures prepared are tabulated in Table 3-13.

The cups were capped and then placed into a rectangular (16.9 × 30.5 cm) plastic box containing ca. 0.5 cm DI water. Another box (of same dimensions) was placed over the first box and the boxes were sealed together using duct tape. The curing box was then stored at 21°C.

Table 3-13. Grout mixtures prepared on June 30, 2003.

Sample Code	Slurry Type/Weight (g)	Grout Cup Number
B-L	Low oil, 85.31	B1
E-L	Low oil, 85.40	E1
B-H	High oil, 85.49	B2
E-H	High oil, 85.39	E2

Another pair of samples was prepared using 80 mL each of treated slurry from Test Run F5 (i.e., 8 hr at 80°C and 500 mL H₂O₂). Sample details are shown in Table 3-14.

Table 3-14. Grout mixtures prepared on July 1, 2003.

Sample Code	Slurry Type/Weight (g)	Grout Cup Number
F5-GRB	F5 run, 83.25	B3
F5-GRE	F5 run, 81.74	E3

These samples were placed in the curing box, which was then resealed and not reopened until the morning of July 8, 2003. The contents of each cup were characterized as to color (using Munsell color charts), odor, and presence or absence of standing water on grout surface. The cups were returned to the curing box until the morning of July 11, 2003. A handheld mortar penetrometer (Soiltest, Inc.) was used to estimate each sample's compressive strength (in lb/in.²).

Top and side view color photographs (digital) were taken of the grout samples and are shown on Page 5 of Appendix F. Finally, the samples were transported to the HKM Engineering Analytical Laboratory for extraction and analysis of mercury and chromium using EPA/SW846 Methods 1311 and 6010B, respectively (refs. 14, 15).

A second phase of posttreatment slurry solidification was initiated on August 5, 2003. This effort included preparation of grout mixtures B5 and E5 (Table 3-15), followed by preparation of selected slurry/grout mixtures (Table 3-16).

The slurry samples were taken from the refrigerator and warmed to approximately 19.3°C (air temperature was approximately 28.3°C) before mixing with grout; slurry aliquots were 80.0 mL, except for F9 (80.1 mL). The above samples were placed in the curing box, under the same conditions as used for the first grout batch, and not reopened until the afternoon of August 12, 2003. The contents of the cups were characterized/photo-documented as before, including TCLP metals extraction/analysis at HKM Engineering Analytical Laboratory. The sample photos are shown on Page 6 of Appendix F.

Table 3-15. Composition of grout mixtures B5 and E5.

Part A. "B" Mixture (g)		Part B. "E" Mixture (g)	
Component	B5	Component	E5
PCT-V/II	9.61	PCT-III	60.00
Fly ash	55.20	Silica fume	18.00
Slag	55.20	Slag	42.00
Total	120.01	Total	120.00

Table 3-16. Grout mixtures prepared on August 5, 2003.

Sample Code	Slurry Type/Weight (g)	Grout Cup Number
F8-E4	F8 run, 82.42	E4
F9-E5	F9 run, 82.76	E5
F9A-B4	F9A run, 82.12	B4
F12-B5	F12 run, 82.02	B5

3.5.2 Results

Physical observations made on the first batch of cured grout samples are summarized in Table 3-17. All samples comply with the ICDF waste acceptance criteria of no freestanding liquid plus compressive strengths of at least 60 lb/in.² (Ref. 6).

Table 3-17. Physical properties of the June 30 through July 1, 2003, grout samples.

Sample Code (Cup Number)	Odor	Munsell Color ^a	Free Liquid	Compressive Strength (lb/in. ²)
B-L (B1)	None	Grayish green (5G 3/2 through 5G 4/2) from side and light greenish gray (10Y 7/1) from top	None	> 150
B-H (B2)	None	Same as for B-L	None	> 150
E-L (E1)	Slight cement-like odor	10Y 7/1 from top and side	None	> 150
E-H (E2)	Cement-like odor	Same as for E-L	None	> 150
F5-GRB (B3)	Organic (petroleum) odor	Dark grayish green (5G 2.5/2) from side and 10Y 7/1 from top	None	> 150
F5-GRE (E3)	Cement-like odor	Light gray (N7) from top and side	None	> 150

a. Munsell Color Name Diagram No. 1 for Gley soils.

The TCLP extraction and analysis results are presented in Table 3-18. The data indicate that both grout formulations meet the UTS levels of 25 µg/L for mercury and 600 µg/L for total chromium (Ref. 3). Comparison of these results to those shown in Table 3-15 document the environmentally significant reduction (to levels an order of magnitude below regulatory levels) in dissolved metals following grout stabilization of these surrogate wastes. Furthermore, extractable-metal levels associated with the “B” mix are at or below the respective IDLs (see Table 3-19).

Table 3-18. TCLP extraction/analytical results for the June 30 through July 1, 2003, grout samples.

Sample Code (Cup Number)	Analytical Results (µg/L)	
	Total Chromium ^a	Mercury ^b
B-L (B1)	<10	<0.1
B-H (B2)	<10	<0.1
E-L (E1)	55	1.1
E-H (E2)	71	0.5

Table 3-18. (continued).

Sample Code (Cup Number)	Analytical Results (µg/L)	
	Total Chromium ^a	Mercury ^b
F5-GRB (B3)	<10	0.1
F5-GRE (E3)	17	0.1

a. IDL = 10 µg/L, 98.3% recovery of the laboratory control standard (LCS) (400 µg/L) and 89.0% recovery of spike (200 µg/L to B-L sample).

b. IDL = 0.1 µg/L, 102.1% recovery of LCS (7.0 µg/L) and 106.0% recovery of spike (1.0 µg/L to B-L sample).

Table 3-19. Dissolved metals levels in the ungrouted surrogate waste slurries.

Sample Code	Analytical Results (µg/L)		
	Total Chromium ^a	Mercury ^b	Comments
L0-M	298,000	200,000	Low oil posttreatment surrogate
F-5-MH	312	37,900	Posttreatment sample from Test Run Number 5

a. IDL = 10 µg/L, 99.8% recovery of the LCS (500 µg/L), 3.3% relative percent difference (RPD) for laboratory duplicate analysis of F-5-MH, and 105.9% recovery of spike (2,000 µg/L) from F-5-MH.

b. IDL = 0.1 µg/L, 96.3% recovery of LCS (70 µg/L), 1.6% RPD for Sample F-5-MH, and insufficient spike (1 µg/L) to calculate percent recovery.

The physical properties of the second set of grout samples are shown in Table 3-20. Inspection of these results indicates that:

- For 500-mL peroxide dosing at 80°C and 8 hr treatment time, the “E” mix produces a harder product with less swell than does the “B” mix (i.e., E4 versus B4); while
- It is not obvious why an extra 4 hr of reaction time results in “B” mix failure to meet the free liquid criterion (i.e., B5). More testing would be required to determine if this would be a consistent problem with using this grout formulation to stabilize the reaction products.

Otherwise, all grout mixtures meet the compressive strength criterion of 60 lb/in.² for placement in the ICDF.

Table 3-20. Physical properties of the August 2003 grout samples.

Sample Code (Cup Number)	Odor	Color	Free Water	Grout Volume (Approx. mL)	Compressive Strength (lb/in. ²)
F8-E4 (E4) 80/500/8	None	Pinkish white (2.5YR 8/1-8/2) from top, with shiny, uncracked surface. Dark greenish gray (Gley 1, 5G 4/1) bottom layer and white-pinkish white (5YR 8/1-8/2) top layer, when cup viewed from side	None	115	≤ 1-mm depression at approximately 1,500 lb/in. ² (hard monolith)

Table 3-20. (continued).

Sample Code (Cup Number)	Odor	Color	Free Water	Grout Volume (Approx. mL)	Compressive Strength (lb/in. ²)
F9-E5 (E5) 80/400/8	None	Very pale brown (10YR 8/2) from top, and mostly gray (10YR 6/1) from side; surface not as shiny as for F8-E4. Greenish gray layer on bottom-most 1 cm of cup (Gley 1, 10GY 10/1)	None	130	Partial imprint (“scratch”) of needle circumference on grout surface, so estimate at approximately 1,500 lb/in. ² (hard monolith)
F9A-B4 (B4) 80/500/8	Very slight cement odor	Very pale brown (10YR 8/2) from top. When viewed from side, mottled dark greenish gray (Gley 1, 5GY 4/1) in lower layer and light grayish-brown (10YR 7/2) upper layer	None	180	Very slight, partial imprint of needle circumference at 150 lb/in. ² ; full penetration (13 mm) of needle at approximately 1,500 lb/in. ² , and partial (7 mm) penetration at approximately 750 lb/in. ² (hard monolith)
F12-B5 (B5) 80/500/12	Cement-like odor	Upon removal of water layer, dark grayish green (Gley 1, 5G 2.5/2 to 5G 3/2) when viewed from top and side. Shiny surface with reddish streaks (of grout?)	Approximately 4 mm (9.2 mL) of slightly cloudy water, decanted off and discarded	110	Based on depth of needle imprints, strength is >750 lb/in. ² , and approaching 1,500 lb/in. ² ; appears to be a hard monolith, even though wet

The TCLP extraction and analysis results are present in Table 3-15. Inspection of these data indicates that both grout mixes consistently achieve compliance with the UTS limits for total chromium and mercury. However, the “B” mix appears to be more effective than the “E” mix for stabilizing chromium, and possibly mercury, as well (Tables 3-18 and 3-21). Photographs showing the grout samples are presented in Appendix F.

Table 3-21. TCLP extraction/analytical results for the August 2003 grout samples.

Sample Code (Cup Number)	Analytical Results (µg/L)	
	Total Chromium ^a	Mercury ^b
F8-E4 (E4)	10	0.3
F9-E5(E5)	47	0.2
F9A-B4 (B4)	<10	0.1
F12-B5 (B5)	<10	0.2

a. IDL = 10 µg/L, 96.8% recovery of the LCS (400 µg/L) and 96.5% recovery of spike (200 µg/L to F8-E4 sample); relative percent difference of 51.9% (i.e., 10 versus 17 µg/L) for duplicate analyses of F8-E4.

b. IDL = 0.1 µg/L, 98.4% recovery of LCS (7.0 µg/L) and 115.0% recovery of spike (10 µg/L to F8-E4 sample); relative percent difference of 1.1% for duplicate analyses of F8-E4.

3.6 Corrosion Test Results

The V-tanks may be used for short-term storage of acidic (pH 3.0 to 3.5) reaction products from chemical oxidation of the mixed waste slurry. The tanks were constructed from Type 304L stainless steel, and were used to collect liquid mixed wastes (pH approximately 8) from 1958 to 1985; no leakage was reported during or after their service life.

TO5 requires evaluation of the respective durability of candidate alloys exposed to a posttreatment surrogate solution to identify the preferred material of fabrication for the chemical oxidation process equipment. In addition, TO5 required assessment of whether the treatment product would have any deleterious effects on the existing V-tank material.

In this study, coupons of the various alloys were immersed in the posttreatment surrogate for almost 34 days at 20 to 25°C. As MSE Technology is not licensed to handle mixed waste, formulation of the surrogate was prepared in consultation with project personnel from the INEEL. The test conditions were judged sufficiently harsh to allow conservative assessment of materials performance, when exposed to treated actual waste(s). These conditions assumed the following:

- 100% conversion of organo-chlorine to free or complexed chloride ion (e.g., Cl⁻ aqueous, HgCl⁺)
- Post-Fenton's pH in the 3.0 to 3.5 range, with no pH adjustment thereafter
- Traces of residual organic matter ($\leq 1,000$ mg oils/kg slurry) and hydrogen peroxide (≤ 400 mg H₂O₂/kg slurry)
- 1:1 weight proportioning between untreated slurry:peroxide (i.e., 50% dilution of initial slurry with H₂O₂ and water-decomposition product).

3.6.1 Corrosion Testing Methods

3.6.1.1 Preparation of the Corrosion Test Rack. The corrosion tests chosen to characterize the corrosive environment of the oxidized waste included: weight loss, visual examination with a low power microscope, stress corrosion cracking, and crevice and pitting corrosion. Type 304L stainless steel was the original tank fabrication material (Type 304L stainless steel). A material less corrosion-resistant (AISI 1010 plain carbon steel) and a material more corrosion-resistant (type 316L stainless steel) were evaluated. The more corrosive material chosen contains approximately 2% molybdenum, giving this alloy improved resistance to pitting and crevice corrosion over that displayed by type 304L.

The test method chosen was a standard rack that contained coupons of the chosen materials for general corrosion, and stainless steel coupons for pitting, crevice, and stress corrosion cracking. A coupon from each of the chosen materials also contained a weld bead through its diameter, as welding was (and will be) the joining process of choice. All samples were placed in a single rack and photographed prior to exposure (see Figure 3-7). Teflon spacers electrically insulated the metal coupons from each other. A certification of chemical composition for all the coupons was received from the coupon supplier.

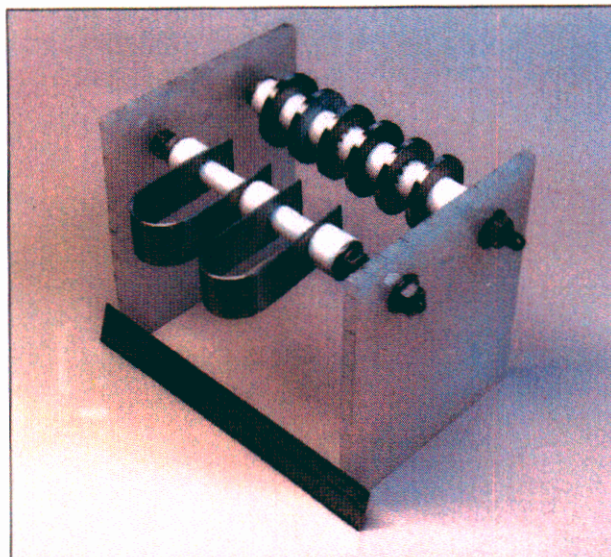


Figure 3-7. Corrosion test rack prior to exposure.

The "U" shaped coupons are for stress corrosion, and slotted Teflon spacers were used to evaluate crevice and pitting corrosion.

The corrosion testing was generally conducted in accordance with the requirements of American Society for Testing and Materials (ASTM) G1, "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens" (Ref. 16).

3.6.1.2 Preparation of the Posttreatment Surrogate Solution and Sludge.

Posttreatment surrogate formulation is shown in Table 3-22. The respective solids were weighed into a clean, dry 5-gal high-density polyethylene (HDPE) pail containing approximately 6.0 kg DI water. The pH was adjusted to approximately 3.42 using concentrated H_2SO_4 ; the surrogate was then brought up to final weight (10.0 kg) with additional water. The completed surrogate's characteristics were: pH 3.66, 31.5°C (due to interactions between the acid and pH 11.6 phosphate solution), and olive yellow (Munsell 5Y 6/8) in color. The contents were mixed well, and the pail then placed in a secondary containment box. The pail was covered with a plastic lid, and the contents allowed to settle/equilibrate over a period of 6 days.

Table 3-22. Posttreatment surrogate slurry composition.

Reagent	Weight (g)
Aluminum chloride • 6 water	8.058
Calcium chloride • 2 water	16.062
Chromium (VI) oxide	10.963
Ferric chloride • 6 water	46.436
Ferrous sulfate • 7 water	50.000
Magnesium oxide	26.039
Manganese oxide	15.238
Silicon dioxide	301.017

Table 3-22. (continued).

Reagent	Weight (g)
Sodium phosphate	434.048
Potassium hydroxide	11.550
Mercuric chloride	2.507
Sulfuric acid (concentrated)	288.0
Oil-peroxide mixture ^a	122.0
DI water	8,676.0
Total	10,007.9

a. Added after immersion of test apparatus, to avoid "coating" the coupons with oil.

Prior to immersing the test apparatus (Figure 3-5) into the surrogate waste, the following activities occurred:

- Determination of supernatant's pH and E_H (i.e., 3.68 and 640 mv, respectively, at 21.0°C)
- Acquisition of raw and 0.45 μm -filtered/acidified (pH < 2) samples for determination of chloride ion/acidity plus dissolved metals levels, respectively.

The test apparatus was carefully lowered into the pail (using plastic straps attached to the test frame) so as to not disturb the underlying sludge layer, followed by addition of the oil-peroxide mixture. The mixture was added after the apparatus, to prevent coating the coupon surfaces with a (potentially protective) layer of oil.

One day after removal of the apparatus, the supernatant's physical characteristics (pH, E_H , color, etc.) were recorded. A second set of raw and centrifuged samples from the supernatant layer was collected; the former sample was for chloride/acidity levels, while the latter was for dissolved metals.

3.6.2 Test Results

3.6.2.1 Corrosion Testing Results. The test rack was placed into the surrogate liquid/sludge mixture for a period of 811.5 hr. This exposure time was chosen because of project administrative constraints, and not as an ideal exposure duration. A photograph of the test rack after placement in the surrogate is shown in Figure 3-8. The rack was lowered into place with the tie wraps that are visible.

A photograph showing the test rack after exposure is shown in Figure 3-9. This photograph shows the test rack immediately after its removal and before it was rinsed in tap water to remove loosely adherent deposits.

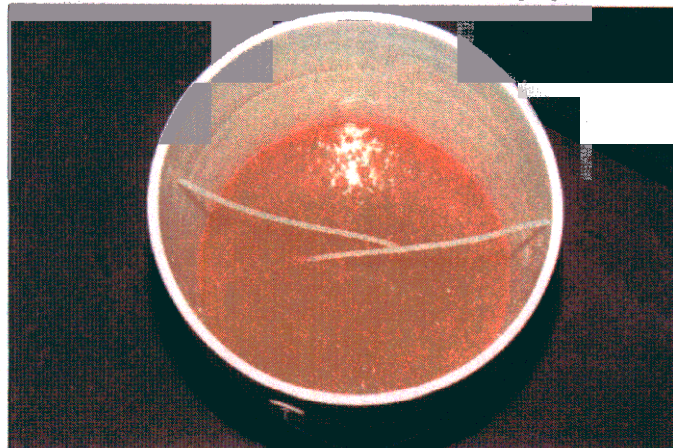


Figure 3-8. Five-gallon bucket containing surrogate mixture and corrosion rack.

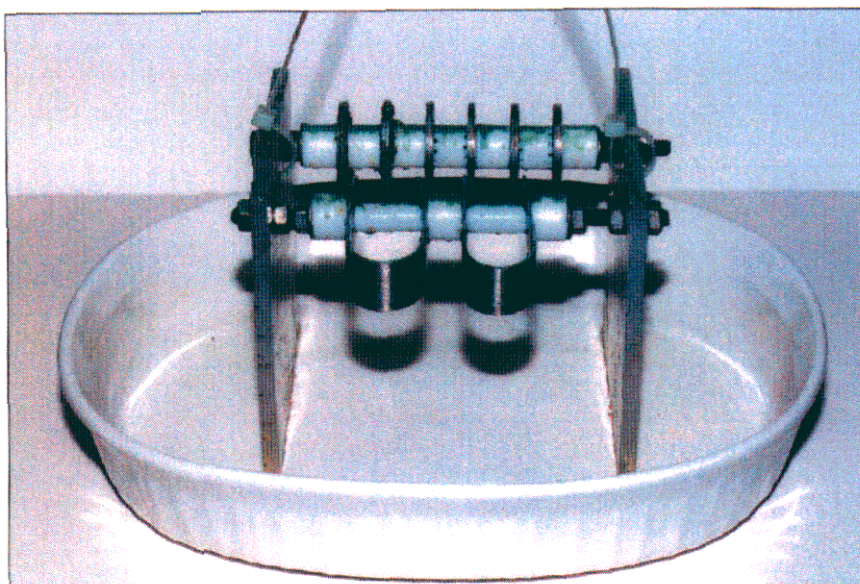


Figure 3-9. Corrosion rack after exposure and before cleaning.

Photographs of the weight loss coupons after their removal from the rack are shown in Figure 3-10.

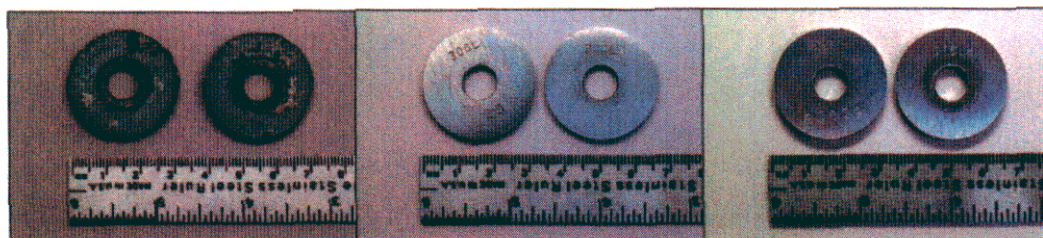
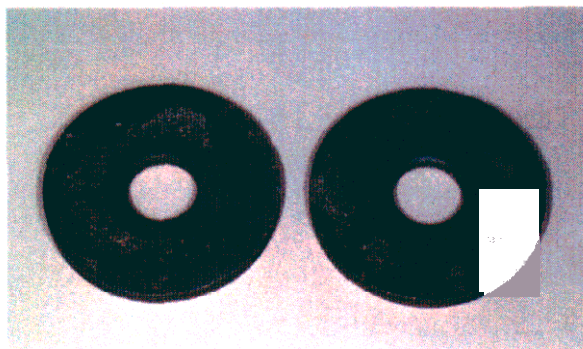


Figure 3-10. General corrosion coupons after removal from rack and before cleaning.

1. **General Corrosion**—After the weight loss coupons were removed from the rack, they were washed in warm water and detergent, and any loosely adherent deposits were removed with a brush. The deposits on the 1010 carbon steel samples were relatively tightly adherent and some had to be scraped with a steel tool to be removed. The samples were then degreased and weighed on an analytic balance. The amount of weight lost during the exposure was recorded and the corrosion rate was calculated per ASTM G1. The only coupons displaying any weight loss were the 1010 carbon steel samples. A



Based upon the weight loss data, the general corrosion rate for the 1010 carbon steel coupons was 5.22 mil per year. However, examination of the cleaned coupons revealed that the primary type of corrosion experienced was pitting, which gives a corrosion penetration rate to perforation by pits that is much greater than the general corrosion rate.

3.6.2.1.2 Stress Corrosion Cracking—The stress corrosion cracking test coupons (types 304L and 316L stainless steel) were examined with a low-power stereomicroscope. No evidence of cracking was observed.

3.6.2.1.3 Pitting and Crevice Corrosion—The areas of the type 304L and 316L stainless steel general corrosion coupons that were covered by special Teflon washers designed to simulate a crevice were also examined with a low power stereomicroscope. No evidence of crevice or pitting corrosion was observed.

3.6.2.2 Supplemental Observations. Corrosion tests at the MSE Technology Analytical Laboratory were performed at ambient temperature (20–25°C). The test results cannot be used to determine if the existing V-tanks could be used as reaction vessels. The temperature increase from roughly 20–80°C would have an impact on the materials. More specifically, these results do not apply to stress corrosion cracking which would be expected to increase dramatically at 80°C. Use of the existing V-tanks as reaction vessels is problematic in any event because it would be difficult to heat the tank(s).

Several hours after addition of the oil-peroxide mixture to the surrogate, surface coloration had changed from light olive yellow (Munsell 2.5Y 5/6) to dark grayish green (5G 2.5/2). Significant gas generation was also evident. It is suggested that the degraded oil reduced the (initial) $\text{Fe}^{+3}/\text{Cr}^{+6}$ ions to $\text{Fe}^{+2}/\text{Cr}^{+3}$ ions; unfortunately, gas composition (e.g., hydrogen) was not determined.

Posttest sampling of the supernatant occurred 1 day after removal of the test apparatus from the surrogate liquid. Oil globules still covered much of the liquid's surface; gas generation continued, although to a lesser degree than observed at the beginning of the test. Physical characteristics of the raw supernatant included pH of 4.34, E_H of 414.5 mv, and grayish-green coloration (2.5GY 7/6).

A comparison of the water chemistry conditions before and after the coupon immersion test is shown in Table 3-23. Acidity refers to calcium carbonate requirements to neutralize the liquid (to pH 7.0), while only dissolved phase (versus total) metals levels were measured in these samples. The only notable change over time is the decrease in dissolved chromium level. Given the changes in pH (from 3.7 to 4.3) and E_h (from 640 to 414 mv), it is suggested that chromium is precipitating out of solution (possibly as a phosphate salt).

Table 3-23. Pretest and posttest water chemistry characteristics (mg/L).

Parameter	Sampling Period	
	Pretest (June 17, 2003)	Posttest (July 22, 2003)
Acidity	10,800	9,720
Chloride	2,820	3,780
Aluminum	1.3	< 0.59
Calcium	426	363
Chromium	272	1.4
Iron	0.47	0.60

Table 3-23. (continued).

Parameter	Sampling Period	
	Pretest (June 17, 2003)	Posttest (July 22, 2003)
Magnesium	1,340	1,300
Manganese	411	341
Phosphorus (phosphates)	7,410	6,810
Potassium	679	571
Silicon	53.0	54.8
Sodium	18,600	17,200
Sulfur (sulfates)	11,500	11,500

4. QUALITY ASSURANCE

Analytical procedures for all instrumentation followed the quality requirements of referenced methods and the manufacturer's specifications. Generally, these consisted of calibrations before, during, and after the analyses and the use of external standards and blanks.

4.1 Bench-Scale Quality Summary

Quality control for the bench-scale portion of the experiments are required for:

- pH measurements
- Temperature readings
- Hydrogen peroxide concentration
- Weight measurements
- Flow measurements
- Gas composition
- Time measurements.

4.1.1 pH Measurements

A pH meter capable of measuring values to ± 0.01 units was used. The pH probe was calibrated using two fresh pH-buffer solutions that bracket the expected pH. The meter was calibrated at the beginning of each test, and calibrations were documented in the project logbook. The pH buffers were measured after the test to verify that calibration was still valid.

4.1.2 Temperature Readings

Temperature readings were performed in liquid and matrices and on solid surfaces. Measurements were performed using thermometers and thermocouples. Temperature controllers, thermocouples, and thermocouple meters are calibrated annually. This equipment had valid calibrations.

4.1.3 Weight Measurements

Analytical balances were used for weight measurements. Several balances are available at MSE Technology with various capacities and resolution. The balances are calibrated yearly at a National Institute of Standards and Technology-approved secondary standards laboratory, and monthly onsite, using a set of calibration weights.

4.1.4 Volume Measurements

Liquid volumes were measured using volumetric glassware for large volumes (≥ 10 mL) and pipettes and syringes for smaller volumes (< 10 mL). Syringes and pipettes were calibrated using deionized water and an analytical balance.

4.1.5 Oxidizer Flow Rate

Hydrogen peroxide was injected using a syringe pump. The syringe pump was factory calibrated and considered accurate without further calibration.

4.1.6 Noncondensable Gas Flow Rate

The noncondensable gas flow rate was measured using a bubble meter. The bubble meter was factory calibrated and considered accurate without further calibration.

4.1.7 Gas Composition Sampling

Gas composition samples were collected at two points in the test apparatus. Gaseous aliquots were collected from the sample ports using gastight syringes. Syringe samples were analyzed in accordance with the requirements of EPA Method 18, "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography," (Ref. 17) using an Agilent/Hewlett Packard 6890 PLUS GC with a thermal conductivity detector (TCD), or by Agilent/Hewlett Packard 6890 GC coupled to a Hewlett Packard 5972A mass-selective detector. Quality assurance and quality control requirements of Method 18 were adhered to during the testing. Additional guidance was obtained from SW-846 Method 8000B, *Determinative Chromatographic Separations*, (Ref. 18).

An on-site GC/MS was used to analyze syringe samples for TCE, TCA, and PCE. Before performing analyses, the GC/MS was calibrated with three standards and a blank, encompassing the concentration range of interest. Only values within the calibration range were reported.

A blank and midrange-calibration-check sample was analyzed at the start and end of each analytical run, and after every 10 samples. The results of the calibration and blank checks are summarized in Table 4-1.

Table 4-1. Summary of QC checks for GC/MS analysis at MSE Technology.

Sample Identifier	O ₂ (ppmv)	CO ₂ (ppmv)	TCA (ppmv)	TCE (ppmv)	PCE (ppmv)
QC Checks Method Validation					
25 % cal	294,679	28,131	58	66	55
25% cal actual	223,713	23,614	64	66	58
% Recovery	132%	119%	92%	100%	95%
25 % cal	350,644	32,794	56	69	51
25% cal actual	223,713	23,614	64	66	58
% Recovery	157%	139%	88%	105%	87%
Calibration Checks F-10 (80°C, 400 mL H ₂ O ₂ , 12 hr)					
10% cal check	65,303	7,908	25	27	22
10% cal actual	89,485	9,446	26	26	23
% Recovery	73%	84%	98%	101%	96%
10 % cal check	173,050	10,975	25	26	23
10% cal actual	89,485	9,446	26	26	23

Table 4-1. (continued).

Sample Identifier	O ₂ (ppmv)	CO ₂ (ppmv)	TCA (ppmv)	TCE (ppmv)	PCE (ppmv)
% Recovery	193%	116%	98%	99%	97%
10% cal check	144,990	10,559	25	26	23
10% cal actual	89,485	9,446	26	26	23
% Recovery	162%	112%	98%	99%	100%
10 cal check	151,578	10,696	25	26	23
10% cal actual	89,485	9,446	26	26	23
% Recovery	169%	113%	99%	99%	99%
10 % mid cal	252,700	13,337	25	27	23
10% cal actual	89,485	9,446	26	26	23
% Recovery	282%	141%	98%	102%	100%
10 % end cal	133,871	10,340	25	26	23
10% cal actual	89,485	9,446	26	26	23
% Recovery	150%	109%	99%	97%	99%
Calibration Checks F-13 (40°C, 400 mL H ₂ O ₂ , 12 hr)					
10% cal ck	155,362	10,335	26	31	26
10% cal actual	89,485	9,446	26	26	23
% Recovery	174%	109%	102%	117%	110%
10% cal ck	162,029	9,189	32	34	32
10% cal actual	89,485	9,446	26	26	23
% Recovery	181%	97%	125%	129%	137%
10% cal ck	226,417	12,890	32	35	32
10% cal actual	89,485	9,446	26	26	23
% Recovery	253%	136%	123%	133%	138%
10% cal ck	205,916	12,038	32	34	33
10% cal actual	89,485	9,446	26	26	23
% Recovery	230%	127%	124%	130%	140%
10% cal ck	148,293	10,118	32	34	32
10% cal actual	89,485	9,446	26	26	23
% Recovery	166%	107%	126%	129%	137%
Calibration Checks F-21 (80°, 250 mL H ₂ O ₂ , 8 hr)					
10% cal ck	211,645	11,946	27	29	27
10% cal actual	89,485	9,446	26	26	23
% Recovery	237%	126%	105%	111%	116%
10% cal ck	234,918	14,116	27	29	28

Table 4-1. (continued).

Sample Identifier	O ₂ (ppmv)	CO ₂ (ppmv)	TCA (ppmv)	TCE (ppmv)	PCE (ppmv)
10% cal actual	89,485	9,446	26	26	23
% Recovery	263%	149%	105%	110%	119%
10% cal ck	112,453	8,403	27	29	27
10% cal actual	89,485	9,446	26	26	23
% Recovery	126%	89%	106%	109%	118%
10% cal ck	91,107	8,452	27	29	27
10% cal actual	89,485	9,446	26	26	23
% Recovery	102%	89%	106%	111%	117%
Calibration Checks F-16 (80°, 500 mL H ₂ O ₂ , 12 hr)					
10% cal ck	55,522	8,962	28	33	32
10% cal actual	89,485	9,446	26	26	23
% Recovery	62%	95%	111%	124%	136%
10% cal ck	118,824	11,152	29	34	32
10% cal actual	89,485	9,446	26	26	23
% Recovery	133%	118%	115%	130%	139%
10% cal ck	157,231	11,684	30	33	32
10% cal actual	89,485	9,446	26	26	23
% Recovery	176%	124%	118%	124%	139%
10% cal ck	137,972	11,545	28	32	33
10% cal actual	89,485	9,446	26	26	23
% Recovery	154%	122%	112%	123%	140%

For the most part, the QC check recoveries were acceptable for the VOCs. Oxygen and CO₂ concentrations were not as reliable; however, these data were collected using alternate means. All blank results were acceptable for all compounds with the exception of water. This compound consistently appeared at high concentrations in the blanks, indicating the column was saturated with water; subsequently, it was impossible to make quantitative determinations for this analyte. PCE and TCE data for test F-16 (80°C, 500 mL H₂O₂, 12 hr) were consistently biased high based on the QC check results. All VOCs were biased high in the latter part of the test samples, compared with the QC check made early in the run. While this type of drift would normally be a concern, the fact that the samples still showed very little or none of these analytes caused the impact on data quality to be minimal. The only detectable levels of VOCs were noted within the first two hours of sampling. All QC checks for test MV, F-10 (80°C, 400 mL H₂O₂, 12 hr), and F-21 (80°C, 250 mL H₂O₂, 8 hr) are considered acceptable.

4.1.8 Time Measurements

Time was measured using a stopwatch for short time intervals and the laboratory clock for long time intervals. Both time-measuring systems were considered accurate without calibration.

4.2 Analytical Quality Control

Because of problems experienced previously by MSE Technology when analyzing this matrix, BWXT provided organics-related analytical support to this project. Given their experience with actual V-tank waste plus treated waste analyses, BWXT are judged most qualified to perform these services. HKM Engineering Analytical Laboratory performed the remaining analyses (condensate, chloride, grouted sample TCLP analyses).

The data from BWXT and HKM Engineering Analytical Laboratory were of acceptable quality. Low, but acceptable, surrogate recoveries were noted by BWXT for several samples. For very low recoveries (<20%), MSE Technology requested reextraction and analysis.

4.3 Data Handling

4.3.1 Logbook Procedures

Personnel conducting the experiments recorded test activity in bound notebooks. Data were logged or recorded on data collection sheets. Each new test day was identified by the day and date at the top of the logbook page, and the daily activities were listed. Each new entry was designated by a time-of-day entry, and started on a new line; data of sufficient detail were entered to fully describe the activity or data being logged. At the conclusion of each day's activities, the logger provided their initials at the end of the log for that day and placed a diagonal line across the remaining unused page for that day's activities. Calibration data for monitoring/measuring equipment was recorded. Photographs or digital images were taken, cataloged, and retained for future reference. Data recorded included the measurements and observations identified previously and other data judged necessary to reconstruct the experiments.

4.3.2 Bench-Scale Data Handling

For data generated during the tests at MSE Technology, the test engineer and technician have the primary responsibility for obtaining data of acceptable, known, and documented quality. In order to accomplish this, calibration procedures, duplicate analyses, and independent check standards were documented in the field logbook. Printouts of pH, and chloride ion data were also stapled into the logbook.

4.4 Deviations from the Test Plan

As directed by BBWI, the test plan was intended to be flexible in order to allow exploration of alternate reaction conditions to determine effective process conditions that met the required DRE objectives for CFTs. During the course of testing, several changes were made to collect appropriate data to support the achievement of these experimental objectives. The following deviations from the test plan were noted:

- Some 40° test conditions were replaced with 80°C runs when preliminary results indicated that 80°C test temperature was more effective.
- Tests were added that varied the amount of oxidizer addition at the 80°C test temperature. The test plan called for 400 or 500 mL H₂O₂ addition. Before testing was complete, tests were also run with 150, 250, and 600 mL H₂O₂ additions.

5. CONCLUSIONS/RECOMMENDATIONS

Conclusions and recommendations resulting from the cold bench-scale tests are discussed in the following areas:

- Chemical oxidation study
- Definitive tests
- Stabilization study
- Corrosion tests.

A brief discussion of the strategy for scale-up of the process is also given below.

5.1 Conclusions for Chemical Oxidation Study

5.1.1 Shakedown

The reaction products from the shakedown runs were not analyzed for the CFTs; therefore, no information existed about the effectiveness of the selected shakedown test conditions. However, the shakedown runs did validate that the test apparatus would allow test runs at the identified test conditions. A major observation during shakedown was that the runs at 80°C appeared to have completely depleted the peroxide, while the 40°C run had substantial residual peroxide. When it was attempted to stabilize the 40°C product with caustic, the slurry foamed over as the pH was adjusted to 7. This suggests that a scaled-up process will have to ensure depletion of peroxide by raising the temperature and driving it off as oxygen.

Effective process parameters were identified during the cold bench-scale tests at the tested conditions. The following test conditions produced final concentrations of CFTs below UTS limits:

- F-21: 80°C, 250 mL H₂O₂, 8 hr, surrogate included Arochlor 1260
- F-9A: 80°C, 500 mL H₂O₂, 8 hr
- F-22: 80°C, 600 mL H₂O₂, 8 hr, surrogate included Arochlor 1260.

Of all the CFTs used in the surrogate, BEHP seems to be the most difficult to treat to levels below the UTS limit of 28 mg/kg. Even at 80°C test conditions, tests F-10 (80°C, 400 mL H₂O₂, 12 hr), F-12 (80°C, 500 mL H₂O₂, 12 hr), and F-20 (80°C, 150 mL H₂O₂, 8 hr) did not remove BEHP to below the UTS limit. Lack of replication of test conditions and the apparent heterogeneity of the reaction products make it difficult to determine whether BEHP can be consistently removed to below the UTS limit. It should be noted that the grouted sample, rather than the reaction products, would be the final waste form requiring disposal. Based on a 1:2 waste to grout ratio, all BEHP results would be below UTS limits for the 80°C runs except F-20, where only 150 mL H₂O₂ were added.

The behavior of VOCs in the system is still not well understood. While the DREs for the VOCs were all very high, questions remain about whether these compounds were destroyed or merely volatilized. The gas-sampling strategy may have missed the bulk of VOC volatilization due to the low frequency of small sample volumes collected.

The following further testing is recommended to better understand the system:

- Replication of testing with additional CFTs that may represent reaction products from original CFTs.
- Replication of selected test conditions to determine effective conditions for BEHP destruction/removal.
- Evaluation of effective chemical oxidation conditions on actual V-tank waste (i.e., “hot” testing)
- Additional tests at 40°C are necessary to understand the behavior of the system at lower temperatures because ultimately, the V-tank contents will have to be heated from their current storage temperature (approximately 15–17°C).
- Additional tests to determine the effectiveness of subsequent treatments are necessary to indicate the extent of further destruction of CFTs occurs when reacted surrogate is retreated.
- Additional tests to determine treatment effectiveness with a reduced rate of H₂O₂ addition are recommended to determine if peroxide utilization efficiency can be increased.
- Testing with Arochlor 1260, with total PCB analysis of reaction products to give an indication of fate of Arochlor 1260 in the treatment process.
- Scale-up of process to one (20-L) or two (50-gal) scales to determine the scalability of various process parameters (including mixing effects) and confirm DRE with larger total quantities of CFTs are recommended. The larger total quantities of CFTs will provide an opportunity to see detectable quantities of the CFTs in the reaction products which will provide a more definitive calculation of DREs for the CFTs. Tests at a larger scale will also provide an opportunity to have on-line GC/MS analysis to better understand the behavior of VOCs in the off-gas.

5.2 Conclusions for Definitive Tests

The results of tests B-1A and B-1B have shown that the V-tank surrogate is effectively processed to a briny slurry that can be easily grouted and will meet all land disposal regulations.

The ability to reprocess the product of B-1A into product that can be grouted and meets land disposal regulations has been demonstrated by the results of run B-1B. The surrogate feed to B-1A was spiked with COCs in great excess to the anticipated maximum concentrations expected for the V-tanks’ waste.

All COCs, except BEHP, were reduced to concentrations below UTS, and below detection limits in most cases. Residual organic loading was near 200 mg/kg and appeared to consist of a slight oily sheen on the surface of the aqueous layer.

It is apparent that some optimization of BEHP removal is necessary. BEHP was substantially reduced from a loading of nearly 2 g to about 200 mg (310 mg/kg). Overall, BEHP DRE was near 88%. In four of seven previous “F” series runs, BEHP was reduced to near the UTS requirement of 28 mg/kg, which reflects about a 90% DRE. Optimization variables may include extended residence time with additional peroxide injection, incremental catalyst addition, an alternative peroxide injection schedule, or an alternative temperature profile.

TCA appeared to be quantitatively volatilized and TCE partially volatilized in the initial hour of the B-1A run. This behavior reflects the volatiles as they exist in the surrogate; whether this characterizes volatilization from the actual V-tanks sludge will have to be established by bench testing of the actual sludge. PCE appeared to stay within the slurry. Downstream processing will have to be able to oxidize (e.g., via ozonation) or adsorb most of the volatiles loading.

One question facing chemical oxidation development at the outset was whether there would be preferential oxidation of the contaminants of concern. This would be advantageous since they are a small amount relative to the oil. Only in B-1A and -1B have data been available for this. The analysis is an overall measure, since it includes everything that is soluble in hexane. It is assumed to include all organics. The total charge amount of organic for B-1A was 15.3 g. The oil analysis at the conclusion showed 12.58 g, for an overall DRE of 18%. The DRE values for the COC were much higher, indicating a preferential attack on them. At the conclusion of B-1B, the oil analysis showed an overall DRE of 99.44%, suggesting that the additional stage got virtually everything. The 18% DRE number in the first stage bears some scrutiny. If it is assumed that none of the 8.48 g of oil added in the charge are destroyed, and that the COC for which analyses are available are present at those levels, the sum adds up to only 9 g. One possible explanation is that the COC had reacted to intermediate forms that were still present, and detected as organics overall, but not analyzed for specifically. If this is true, then the 99.44% number is all the more encouraging, because it suggests that there are no partially reacted intermediates remaining after the second stage.

Operation at 80°C initial temperature is very stable and does not exhibit autocatalytic behavior. To scale the process, it will be important to maintain the heat removal to heat generation ratio of the bench scale apparatus. Pilot testing of a geometrically similar reactor will be needed to confirm this assumption.

5.3 Conclusions and Recommendations for Stabilization Study

All of the “B” and “E” grout:slurry mixtures evaluated comply with the ICDF’s compressive strength and UTS-related disposal criteria (Ref. 3). Under only one case was there an unexplained failure to meet the “no free liquid” criterion (i.e., F12–B5). More grout testing is recommended to determine if release of free liquid is a consistent problem with this grout formulation and similar reaction products. TCLP metals levels in the B series grout:slurry mixtures were lower than those observed in the “E” grouts. Thus, preference is presently given to use of the “B” grout formulation for stabilization of treated V-tank surrogate slurry.

5.4 Conclusions and Recommendations for Corrosion Tests

- Based upon the depth of the pits observed on the 1010 carbon steel coupons, this material would not be suitable for use in the process tanks or piping that would be associated with the chemical oxidation of V-tanks’ liquids and sludge.
- Since no pitting or crevice corrosion and stress corrosion cracking was observed in any of the stainless steel coupons, the material of choice for process tanks and piping should be type 304L stainless steel. It should be cheaper to procure than type 316L stainless steel.
- The exposure time for the evaluation of stress corrosion cracking, pitting and crevice corrosion was relatively short (approximately 34 days). If the planned exposure time of the chemically oxidized materials increases from months to years, corrosion testing with a longer duration should be planned and executed. This will ensure that corrosion failures do not occur during lengthened exposure times.

Corrosion tests are recommended to determine the impact on selected materials at the process temperature conditions.

5.5 Conceptual Model of Chemical Oxidation Treatment

Based upon the presently available database, MSE Technology suggests the following sequence of events during chemical oxidation of the V-tanks surrogate slurry by Fenton's reagent:

1. Initially, each organic CFT, plus elemental mercury, partitions between the oily, aqueous, and vapor phases, as determined by their respective K_{oc}/K_{ow} , water solubility, and Henry's coefficient for the given matrix at 20–25°C. The portion of each CFT adsorbed onto the surface of an oil droplet is then absorbed into the oily phase, wherein the rate is dependent upon the above parameters. Over time, this diffusion process reduces the CFT's tendency to either dissolve into, or volatilize from, the aqueous phase.
2. At temperatures $\geq 80^\circ\text{C}$, much of the H_2O_2 is degraded to O_2 before it can react with the CFTs; subsequently, there may not be a large "excess" of free radicals in aqueous solution at any moment in time. Furthermore, those radicals present may preferentially attack those chemical bonds most susceptible to oxidation; the suggested order is chlorinated alkenes (TCE, PCE) > ester linkages in BEHP > PCB > chlorinated alkanes \geq non-chlorinated alkanes $\geq \text{Hg}^0$.
3. The polar, partially oxidized reaction fragments containing RCOOH and ROH groups remain in aqueous phase, while the non-polar fragments are re-adsorbed into the oil droplets; of particular interest is the mono-ester of ethylhexyl-phthalate (MEHP), which is probably as recalcitrant to oxidation as are many of the compounds in the background oil phase.

The non-polar CFTs and reaction fragments present in the oil droplets are released into the aqueous phase as treatment proceeds, due to shrinkage of the droplets and exposure of fresh surfaces to chemical oxidation. This treatment cycle continues until the Fenton's reagent is exhausted, and chemical oxidation subsequently stops. Before this time, however, some amount of the organic CFTs are mineralized to water and carbon dioxide. The apparent absence of free chloride ions may be due to mercuric complexes (e.g., HgCl^+ , HgCl_4^{-2}) or halo-carboxylic acids (e.g., chloro-acetate ion).

5.6 Management Implications

The single most important implication taken from this study is that the hydrogen peroxide based chemical oxidation system studied in this testing was able to demonstrate destruction of all CFTs (including Arochlor 1260) with the exception of BEHP to regulatory levels. Although BEHP was not consistently destroyed to regulatory levels, the substantial destruction demonstrated in these tests provide strong evidence to suggest that the process can be refined and/or applied repeatedly to consistently achieve BEHP levels below UTS. Subsequently, management should consider larger reaction vessels than originally anticipated to accommodate hydrogen peroxide volumes in excess of 600 mL per 150 g charge of surrogate and/or incorporating the potential for multiple batch treatments into the design methodology. In addition, such changes may necessitate the need to reevaluate the size and number of holding vessels used to temporarily store treated waste while awaiting chemical analysis results before stabilization. With respect to the DREs calculated as part of this study, it should be noted that these calculations do not consider potential products of incomplete oxidation (e.g., vinyl chloride), which may be regulated and/or may result in the final waste form being characteristically hazardous pursuant to RCRA. For example, although this study estimates Arochlor 1260 destruction in excess of 90%, the products of this destruction

Table 5-1. Summary table of conclusions/inferences related to associated test objectives.

Test Objective	Description	Conclusion	Inferences
TO-1	To determine which of the potential process scenarios are effective in treating surrogated V-tank waste to regulatory compliance levels, and to identify the most favorable conditions for the chemical oxidation process scenario for future pilot-scale testing and field deployment. Initial tests should be performed at the extreme ranges of the most aggressive conditions available to us, and at the minimal conditions that can be reasonably expected to produce results. This will establish bounds within which we can refine the effectiveness of the process.	<p>Within the bounds of experimental design, the most favorable conditions were identified to be:</p> <p>Temperature 80–100°C pH 3–4 H₂O₂ volume 250–600 mL</p> <p>Tests conducted at 40°C were considered ineffective and potentially dangerous due to the accumulation of unreacted peroxide.</p>	No inferences made
TO-2	To determine conversion extent of CFT destruction in the chemical oxidation process (COP). This objective and the following objectives are measurements to be made on both extremes of the process from TO 1, and at a limited number of suitable points in between.	All COCs, except for BEHP in the surrogate waste, were reduced to concentrations below UTS. The DRE for BEHP was approximately 88% on average with approximately 90% DRE required to meet the UTS. There is very high confidence that the process can be refined and/or applied repeatedly to consistently achieve BEHP levels below UTS.	Regression analysis of BEHP DREs vs. total peroxide volume data supported a suspected first-order relationship. Predictions made from this first-order approximation indicate that target BEHP DREs can be achieved with approximately 800 mL of peroxide in a single batch.
TO-3	To estimate the rate of heat generation of the COP.	During the addition of peroxide, which should represent the most extreme case of heat generation, it is estimated that the rate of heat generation is 340 to 1,350 calories per minute.	No inferences made
TO-4	To determine the bulk gas-generation rate of the COP.	During the addition of peroxide, which should represent the most extreme case of gas generation, the gas generation rate is approximately 0.45 g/min (vs. theoretical maximum of 0.565g/min for the given feed rate).	No inferences made
TO-5	To estimate the durability of potential construction materials exposed to the COP.	Tests conducted on 1010 carbon steel showed significant corrosion, indicating that carbon steel is not suitable for process components. Corrosion tests on 304L stainless showed no corrosion at 20–30°C.	No inferences made

Table 5-1. (continued).

Test Objective	Description	Conclusion	Inferences
TO-6	To estimate changes in leachability between raw waste and oxidized waste.	Although this test objective was not directly addressed, the leachability and compressive strength of select CFTs from oxidized and solidified waste forms were measured. Measurements of compressive strength and TCLP levels in two grout formulations (E and B) met ICDF's compressive strength requirements and UTS-related disposal criteria (40 CFR 268.48). TCLP metals levels in the B series grout:slurry mixtures were consistently lower than those observed in the E grouts.	No inferences made
TO-7	To determine the sequence and relative extent of destruction.	VOCs within the surrogated waste can be removed from the waste matrix at 80°C with an oxygen purge stream in 8–12 hr without supplemental chemical oxidation.	Test results indicate that there is preferential destruction of CFTs over oil and preferential destruction of double-bonded VOCs within the class of CFTs.
TO-8	To propose and provide data to support a detailed strategy to prevent autocatalytic reactions for, and Fenton's reagent during active remediation.	Avoid near neutral pH when residual peroxide is present through process and engineering (i.e., redundant block valves) controls. Maintain operations at 80°C or greater during peroxide addition to avoid residual peroxide buildup.	No inferences made
TO-9	To determine the behavior of VOCs in the off-gas; volatilization as opposed to destruction.	No definite conclusions drawn from experimental work.	Based on the demonstrated ability to readily remove the VOCs without chemical oxidants in the shakedown tests, it may be inferred that volatilization dominates oxidation.
TO-10	To determine completion of the destruction of the RCRA hazardous organics and total organics, and to identify real-time methods for determining completion points.	Measurement of carbon dioxide in the off-gas is the best way to infer completion of oxidation in V-tank wastes.	It is inferred that the reaction has proceeded to the extent possible with the reagent added when the bulk off-gas generator rate approaches zero.

may still be classified as PCBs rather than being completely mineralized as may be construed from this estimate. As a result, management should continue to support efforts to ensure potential products of incomplete oxidation are identified and evaluated to the extent practicable in future testing to avoid partial achievement of all regulatory requirements. Another important implication is the fact that VOCs are most likely separable from the overall waste matrix with only air or oxygen sparge at elevated temperatures without chemical oxidants. This has tremendous implications in potentially allowing for a simplified clean-up strategy should the V-tank waste be found to be non-characteristic waste pursuant to RCRA. In addition, the fact that VOCs may be easily removed from the V-tank waste may make more attractive the notion of “in-situ” treatment, as the largest concern of in-situ treatment (i.e., pitting corrosion) will be largely removed by extracting the chloride laden VOCs.

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